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A note on the published results of studies in atmospheric chemistry

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(Meteorological Office)

AIR MINISTRY

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Introduction

1. M.R.P. 993 (1) recommended that the Meteorological Office should participate 'if only for the period of the Geophysical Year' in the programme of chemical sampling of the atmosphere which is now being followed by most countries of north-west Europe under the direction of Professor C. G. Rossby. M.R.P. 993 also stated that 'the value of this work to Meteorology was not yet proved,' and did not express any view as to whether it was desirable or not to maintain sampling stations in normal times.

2. The paper which follows is intended as a basis for a general discussion of policy with respect to chemical sampling. It is evident that sampling is most likely to yield interesting and useful results if it is carried out as a part of a widespread organisation, and therefore especial attention is given to the method now in general use in Professor Rossby's organisation. Other methods which have been, or might be, used are also briefly considered.

3. The technique of sampling now in general use in north-west Europe is an extremely simple one: the rainfall is collected in a funnel, while air is bubbled through a suitable absorbent solution. Both rainwater and solution are subsequently analysed for sodium, potassium, calcium, magnesium, sulphur, chlorine and ammonia, while the rainwater is also analysed for carbonate and nitrate: pH and conductivity are also measured.

4. Such observations are evidently not sufficient for a truly comprehensive study of the chemistry of the atmosphere. None of the major constituents is examined, nor are any chemical processes except those occurring in the lower atmosphere. There are even some known variables in the constitution of the lower atmosphere which are not considered, of which ozone is probably the most important.

5. The somewhat curious range of the subject is a consequence of its history. In the middle of the nineteenth century the scientific basis of plant feeding began to be understood and it was realised that nitrogen compounds were of great importance. It was natural then to enquire whether the plant could be adequately supplied either directly from the air or by salts brought down by the rain. For many years Liebig maintained that a plant could obtain all the ammonia it needed from the air, but his view was not universally accepted and much of the work done in the latter part of the nineteenth century, particularly at the Rothamsted Experimental Station, was concerned with this controversy. Once it was settled, interest in the subject declined: but it has remained, until very recently, the province of the agricultural research worker. Until the 1950s it was concerned almost exclusively with the inorganic chemistry of rainwater: and although the ions present in the free air are now also studied, the literature

of the subject still deals principally with the analysis of rainwater. A comprehensive account of the chemistry of rainwater and a very full list of references is given by Eriksson (2).

6. Meteorologists first began to pay serious attention to atmospheric chemistry because of its evident importance in the study of condensation nuclei. Whereas the agriculturalists had been principally interested in nitrogen compounds, the meteorologists were principally interested in salt. But as soon as the distribution of sodium and chlorine ions in rainfall came to be studied, a very curious fact emerged. The ratio, mass of chlorine to mass of sodium, found in rainwater is (save at one or two places on very exposed coasts) usually substantially less than that found either in pure sodium chloride (1.5) or in sea water (1.8). Moreover, the farther one goes inland, the less the ratio becomes: typically, it is about 1.3 on the west coast of Scandinavia - the only region for which there is yet a substantial body of data - and diminishes to 0.6 or less in the east of Sweden.

7. This was a very unexpected result. That the total mass of salt brought down would decrease as distance from the windward coast increased was evident enough: but it had hitherto been assumed that, at whatever distance, it would still possess its original constitution. It is true that the result might have been explained if, as the salt was washed out of the air, some other sodium salt was progressively added. But there is no obvious source of this other salt in such quantities: moreover, the analyses show no trace of its anion. The only other explanation possible is that the salt removed from the sea is dissociated in some way, in itself a remarkable fact considering the stability of the material. Cauer (3) put forward the hypothesis that the sodium chloride was oxidised by the ozone present in the lower atmosphere, giving first free chlorine and then, by combination with water vapour, hydrochloric acid.

8. Cauer supposed that the hydrochloric acid remained in the air either as a gas or in the form of droplets of solution so small that they did not serve as effective condensation nuclei. Neither of these alternatives appears very attractive at first sight: but one or the other seemed essential to explain the fact that a great deal of the sodium is precipitated within two hundred miles or so of the coast, while the corresponding chlorine is not.

9. Rossby and Egnér (4) followed up the idea. Since the chlorine content of the atmosphere is certainly not increasing steadily, all this excess chlorine must return to earth at some stage. This might occur by direct absorption by the soil or plants: and there is also a possibility that it is precipitated as chlorates or hypochlorates which the sampling technique misses. But the authors dismissed these mechanisms and argued that, since rain in winds straight off the sea brought down excess of sodium, winds from some other direction, or in some other part of the world, must bring down excess of chlorine. They therefore sought for such occasions and found in fact that with southerly winds, which had had a land track of several hundred miles, the Cl : Na ratio was very high, reaching 3.5 at times. On the basis of his results, Rossby distinguishes four zones of chemical climate which are successively farther from the windward coast. These are

(a) A coastal zone where unaltered sea-salt predominates and the Cl : Na ratio in precipitation approaches 1.8.

(b) A zone where the salt is largely dissociated, and little chloride deposited: the Cl : Na ratio is low.

(c) A zone where little sodium remains, and the chloride, in forms other than NaCl, becomes the principal condensation nucleus: the Cl : Na ratio is high.

(d) A zone where most of the ions originating in the sea have already been lost: Cl and Na present are derived from the ground, where sodium is the commoner: the Cl : Na ratio is low, but the amounts of both are very small.

There is solid evidence for the existence of zones (a), (b) and (d) but the evidence for zone (c) is much less good, and the explanation which Rossby advances is largely hypothetical.

10. Meanwhile Junge (5) in America has worked on rather different lines. He has hitherto used only single observing posts, but his analyses have been more penetrating. Two classes of nuclei were separated out by a cascade impactor and analysed separately. These were 'giant nuclei' (0.8 to 8μ diameter) and 'large nuclei' (0.08 to 0.8μ diameter). At the same time, air from which virtually all particles had been removed by a millipore filter was analysed. Junge found that in the maritime air the Cl : Na ratio for giant nuclei was always substantially the same as in sea water, whereas in the large nuclei the ratio is much lower - about 0.5. Evidently, if we assume that the giant particles are precipitated earlier than the large particles, Junge's results go some way towards explaining the variable Cl : Na ratio without the necessity to assume dissociation at all. However, they do not provide a complete explanation because the total amount of Cl and Na in the large particles, per cubic metre of air, is far too small. Even more remarkable is Junge's discovery that the amounts of NH_3, SO_3 and SO_4 ions present in gaseous form are about ten times greater than the amounts present as nuclei, while the amounts of chlorine are about the same in the two forms. Evidently there are possibilities here of quite complex interactions and it is unsafe to interpret results in terms of water and salt, even dissociated salt, only. Junge also found very high concentrations of Cl, SO_4, NO_3 and NH_4 in the air near Frankfurt: but in this case they were mainly in the large nuclei. Junge concludes indeed that 'Almost all the large ions are of continental origin, even over the oceans' - a remarkable generalization. He remarks further, 'A real step forward in the understanding of the basic processes of air chemistry can be gained only if aerosols and gases are measured simultaneously but separately and if the aerosols, in turn, are separated according to size.'

11. One other conclusion of Junge's has a special interest: he believes that almost all the NO_3 in the atmosphere originates on the coast-line, which thus constitutes a 'line source'. The analysis of concentrations at various heights, using isolated mountains as sampling stations, might make useful contributions to the study of long range diffusion.

Discussion

12. A system of chemical analysis of the air should aim at the elucidation of at least the following questions -

(a) How and where are the 'chemical constituents' - using the term in the narrow and arbitrary sense discussed in paragraphs 3 to 5 - introduced into, or formed in, the air?

(b) How do they react, both chemically and physically, with each other and with the major constituents - oxygen, nitrogen, carbon dioxide and water in all its phases?

(c) How are they removed from the atmosphere?

(d) What are the effects of their variations on the other meteorological processes, particularly those of cloud-formation and precipitation?

13. A consideration of these requirements, particularly (a) and (c), at once suggests the absolute necessity of an extensive network of observing stations; there can be no other satisfactory means of identifying either the 'sources' or 'sinks' of material. Moreover, since there can be little doubt that rainfall is the most important 'sink' a study of the constitution of rain water is a necessary part of the investigation. In these respects, Rossby's methods have the advantage over Junge's. On the other hand, Junge's methods are probably the more powerful in the study of chemical processes in the atmosphere.

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14. It is evident that there would be very great advantages in a combination of the two procedures, provided that the cost and problems of sampling were not prohibitive. A network such as this, yielding analyses of air, rain, and two sorts of aerosol would be in some danger of providing unmanageably large amounts of data: yet it would be by no means exhaustive. There are a number of additional quantities which could be measured, or additional refinements which could be made in the procedure and which may well be essential to the solution of the problem. The following are all theoretically possible extensions of the technique and, indeed, useful work has already been done on most of these lines of investigation.

(a) The period of sampling might be reduced, so that results for a particular synoptic type could be more readily isolated.

(b) The variations of chemical constituents in the vertical might be measured, e.g. by the systematic use of mountain stations, by balloons or aircraft.

(c) Ozone, carbon dioxide and possibly other gases now outside the scope of the investigation (e.g. methane) might be determined. (Measurements of ozone and CO_2 are of course made but they are not integrated into this investigation, although ozone is generally considered to play a vital role in atmospheric chemistry.)

(d) It is possible that useful additional information on the gaseous components could be obtained by spectroscopic methods.

(e) Junge's division of the aerosols into two size-classes and the point of division are somewhat arbitrary. It would appear desirable to discover how many chemically distinct classes there are and the best points of division: and to base further routine observations on this classification.

(f) Electrical conductivity of the atmosphere and ionic mobilities might be measured.

(g) The chemical content of rainfall might be studied in relation to drop-size, somewhat in the manner of Turner's work (6). Indeed, some study on these lines appears to be essential before any estimate can be made of the relationship between the mass of matter in suspension in the air and the rate at which it is brought down by rainfall. Turner did not measure the quantities in suspension, but his results clearly indicate that the relationship is not a simple one. Some improvement of his analytical technique would be necessary, since his assumption of a constant Na : Cl ratio is, as already shown in earlier paragraphs, no longer tenable.

15. The discussion of the last two paragraphs has related to questions (a), (b) and (c) of paragraph 12. With regard to question (d) - what are the effects of the chemical constituents on general meteorological processes? - it seems probable that ideas on the nature of condensation nuclei and perhaps of freezing nuclei will be profoundly influenced by the results of these chemical studies, and it is possible that the methods of atmospheric chemistry will have important applications in the study of long range diffusion. At all events, no theory of long range diffusion would be acceptable unless it were compatible with the observed phenomena of atmospheric chemistry. It is difficult to see how the influence of the subject could extend much farther than this in other fields of pure meteorology, although it is no doubt important in studies of meteorology applied to such subjects as agriculture, the deterioration of materials, and perhaps public health.

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16. Any elaborations of the sampling technique, such as those discussed in paragraph 14, would be most productive if they were adopted by a selection of stations throughout the whole international observing network. It does not follow, however, that it is useless to discuss their application at British stations acting independently: indeed, since any of them would be fairly expensive, the international organisation would probably be reluctant to adopt them unless they had been tried out and shown to be essential or at any rate very valuable.

It would therefore be possible for valuable work to be done within the Meteorological Office on the subject of atmospheric chemistry, quite apart from any participation in the international system. But some expense would be entailed and, more important, at least one scientific officer would have to be directed to this work. Mere participation in the existing system of observation, on the other hand, entails little outlay either in money or time.

Summary

The studies in atmospheric chemistry which have been made in the last few years have led to a number of discoveries of great intrinsic interest, and have set a number of attractive problems. Most of these belong to the subject itself, but they have a limited importance in other branches of meteorology.

It would be possible for the Meteorological Office to participate in the existing network of observing stations in north-west Europe without any important outlay in money or time. This network has made great contributions to the subject, and its usefulness is certainly not yet exhausted; but the sampling technique is rather crude, since it does not permit the contribution to the sample of the gaseous ions and of the various classes of particle to be distinguished. It is likely that the need for an improved technique will be felt more and more in the next few years and there is scope here for much useful work, if the time could be found for it.

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